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(54) Title: REACTIVE MATRIX FOR REMOVING MOISTURE FROM A FLUORINE CONTAINING GAS AND PROCESS

(57) Abstract

A process and composition for removing moisture from a NF_3 or F_2 gas wherein the gas is contacted with alumina particles coated with aluminum trifluoride. The aluminum trifluoride is formed by reacting alumina particles with an aqueous solution of hydrogen fluoride.

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REACTIVE MATRIX FOR REMOVING MOISTURE FROM A FLUORINE CONTAINING GAS AND PROCESS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a reactive matrix and a process for removing impurities from a fluorine containing gas. More particularly this invention relates to a reactive matrix and a process for removing moisture from nitrogen trifluoride gas or fluorine gas while avoiding undesirable exothermic reactions.

2. Description of Prior Art

At the present time, a wide array of supports for a reactive matrix are utilized to remove impurities from nitrogen trifluoride gas. A major problem with presently available reactive matrices is that some of the impurities in the nitrogen trifluoride such as N_2F_2 and N_2F_4 are not compatible with some of the supports presently used. These impurities decompose exothermically to catalyze the decomposition of NF_3 which, in turn, causes a cascade of reactions that results in undesirably high temperatures which may even destroy the housing utilized for the reactive matrix. It has been observed by Broer et al, J. Mater. Res., 1988, 3(4), 755 that reaction of components of NF_3 gas with alumina did not occur until 650°C. The reaction of nitrogen trifluoride with alumina at temperatures greater than 650° C were shown by FTIR and subsequent analysis to produce nitrosyl fluoride (NOF), NO_2, NO and AlF_3.

It also has been shown in Japanese patent 01261209 (1989) that the purification of NF_3 with previously dehydrated alumina within a temperature range of 0 to -125°C removes impurities of N_2O, CO_2 and N_2F_2. The cold temperature minimized the adsorption of NF_3 onto the alumina support.

Japanese patent 0203450 A2 (1990) discloses that purification of NF_3 in stages prevents any temperature increases and subsequent explosions. N_2F_2 and N_2F_4 are first removed by passing the NF_3 gas through a metallic tube, e.g. stainless steel or Monel, at 150 - 300°C. Subsequently, OF_2 is removed by bubbling the gas through an aqueous solution containing Na_2SO_3 and Na_2S. The purified NF_3 then flows through a previously activated alumina layer for removal of N_2O and CO_2. Both of these impurities are present in concentrations higher than water.

U.S. Patents 4,853,148 and 4,925,646 disclose the use of aluminum trifluoride on an alumina support to remove moisture from a hydrogen halide gas. The aluminum trifluoride is formed by reaction of corresponding partially or fully alkylated compounds and/or pendant functional groups with the corresponding gaseous hydrogen halide. The partially or fully alkylated compounds are utilized as a solution in an organic solvent. Formation of aluminum trifluoride or aluminum by this process results in trace amounts of organic moieties or compounds being present on the resultant product. Even trace amounts of organics on a material used to purify NF_3 are undesirable since they react with NF_3 or impurities in NF_3 in an exothermic reaction which generates sufficient heat to cause further undesirable reaction of the NF_3.

In addition, formation of AlF_3 via reaction of the starting material, AlR_3, where R is an organic moiety, is not practical with gaseous HF since gaseous HF has a low vapor pressure and excess unreacted HF is difficult to remove from the support. Furthermore, formation of AlF_3 from aluminum hydride and HF gas cannot be done with HF in aqueous solution since water reacts with aluminum hydride.

Accordingly, it would be desirable to provide a scavenger for moisture in NF_3 which does not react with NF_3 or with impurities normally found in NF_3. In addition, it would be desirable to provide such a scavenger which does not react with compounds which are adsorbed by the scavenger.

SUMMARY OF THE INVENTION

The present invention provides particulate composition, a process and an apparatus for removing moisture from a gas containing fluorine gas or nitrogen trifluoride gas while avoiding undesirable exothermic reactions. The apparatus of this invention comprises a housing containing a particulate composition which is an active scavenger for removing moisture from NF_3. The housing includes an inlet for feed NF_3 and an outlet for treated NF_3. The particulate composition comprises particles formed from alumina coated with AlF_3 which is formed by reacting alumina particles with an aqueous solution of hydrogen fluoride (HF). Alternatively, the AlF_3 -coated alumina particles can be formed by the controlled reaction of alumina particles with gaseous HF or HF/inert gas mixtures. AlF_3 particles formed in this manner are free of moieties, such as organic moieties which are reactive with either F_2, NF_3 or impurities normally found in F_2 or NF_3.

Moisture removal from F_2 or NF_3 is effected by passing the F_2 or NF_3 gas through a bed of the particles under conditions to effect adsorption of moisture from the NF_3. The adsorbed moisture is

chemically bound in hydrate formation with the aluminum trifluoride. The alumina particles also adsorb oxides of carbon, i.e., carbon monoxide and carbon dioxide, when these oxides are present in the gas. The alumina particles additionally will remove trace levels of HF gas in NF_3 via chemisorption to produce additional AlF_3 and moisture. The generated water vapor will be scavenged by the reactive matrix. Since the particles prepared in accordance with this invention do not react exothermically with compounds normally found in NF_3 gas, removal of the moisture from NF_3 is effected without a significant increase in temperature or pressure.

BRIEF DESCRIPTION OF THE FIGURES

Fig. 1 is a schematic drawing of an apparatus of this invention.

Fig. 2 shows the change in temperature and pressure over time when treating NF_3 to remove moisture in the apparatus of this invention.

DESCRIPTION OF SPECIFIC EMBODIMENTS

In accordance with the process of this invention, a gas containing fluorine gas or NF_3 gas is contacted with particles of an alumina support coated with aluminum trifluoride made by reacting alumina particles having an average size between about 0.1 and about 10 mm preferably between 1.0 and 5.0 mm with an aqueous solution of hydrogen fluoride until substantially the entire surface of the aluminum particles is coated with AlF_3. Reaction is conducted with an aqueous solution containing between about 1% and about 10%, preferably between about 3% and about 5% hydrogen fluoride at a temperature between about 0°C and about 40°C, preferably between about 20°C and about 30°C. The particles then are recovered and dried to remove any moisture therein. Typical drying conditions comprise a temperature greater than 100°C and preferably greater than 200°C.

The NF_3 or F_2 can be treated alone or in admixture with an inert gas such as argon, neon or xenon.

The moisture removal capacity or efficiency of the active scavenger for removing moisture is not affected by the presence of other impurities such as oxides of carbon that would preferentially compete with moisture for binding to the support. In addition, the particles of alumina coated with aluminum fluoride prepared in accordance with this invention are capable of adsorbing moisture from F_2 or NF_3 gas without reacting with impurities normally found in NF_3 or F_2.

Fig. 1 illustrates the use of the present invention. Referring to Fig. 1, an apparatus of this

invention 10 includes an inlet 12, an outlet 14 and a housing 16. Particles 18 comprise alumina particles coated with AlF_3 prepared by reacting alumina particles with an aqueous solution of hydrogen fluoride.

The following examples illustrate the present invention and are not intended to limit the same.

Example 1

A 50-cc sample of aluminum trifluoride on alumina is prepared according to the following procedure. To aluminum oxide (32.5 g) in a PFA bottle is added a diluted solution of 49% aqueous HF (4.1 ml) in deionized water (50 ml). After three hours, the liquid is decanted and the remaining aluminum trifluoride on alumina is allowed to air dry in the fume hood overnight. The material is transferred to a sample cylinder where further drying and dehydration of the aluminum trifluoride is accomplished at 400°C for three hours under a 3.0-slpm flow of nitrogen.

Example 2

The capacity of the aluminum trifluoride on alumina scavenger for the removal of water vapor is measured according to the following procedure. A 50-cc sample cylinder is filled with the AlF_3/alumina scavenger prepared in Example 1. A test gas mixture of 480-PPM H_2O in nitrogen is passed through the sample tube at a flow rate of 1.0 slpm. The downstream H_2O concentration is measured using an Ametek 5700 Moisture Analyzer. After 2760 min, H_2O breakthrough is detected to provide a H_2O capacity for the inorganic scavenger of 26 L H_2O/L bed.

Example 3

The compatibility of the aluminum trifluoride on alumina scavenger to NF_3 gas is determined according to the following example. A 50-cc sample cylinder is filled with the AlF_3/alumina scavenger prepared in Example 1. The sample cylinder is equipped with a thermocouple inserted through the side via compression fitting to measure the internal temperature of the scavenger. The sample cylinder is installed on a manifold with an optional by-pass loop around the sample. A 200-sccm flow of NF_3 (CP grade) is either passed through the sample cylinder or optionally bypassed (to provide background level). The flow of NF_3 is initiated then passed through the sample and, as shown in Fig. 2., there is no appreciable increase in temperature. The downstream by-passed and purified NF_3 gas spectra are measured using a FTIR and are observed to be identical. The sample is pressurized to 43.30 psia, valved off and left static overnight. The pressure remains constant overnight and FTIR analysis of the sample head space shows no generation of impurities.

CLAIMS

1. A particulate composition suitable for removing moisture from a gas selected from the group consisting of nitrogen trifluoride gas and fluorine gas, which comprises:

particles of alumina having a coating of aluminum trifluoride,

said coating being formed by reacting particles of alumina with an aqueous solution of hydrogen fluoride followed by drying the alumina particles coated with aluminum trifluoride.

2. The process for removing moisture from a gas selected from the group consisting of nitrogen trifluoride gas and fluorine gas which comprises intimately contacting said gas with the composition of claim 1 and recovering said gas after contacting with composition of claim 1.

3. An apparatus for removing moisture from a gas selected from the group consisting of nitrogen trifluoride gas and fluorine gas which comprises a housing containing the composition of claim 1, an inlet into said housing and an outlet from said housing.

4. The process of claim 2 wherein said gas is nitrogen trifluoride.

5. The process of claim 2 wherein said gas if fluorine gas.

6. The process of claim 4 wherein said gas contains an inert gas.

7. The process of claim 5 wherein said gas contains an inert gas.

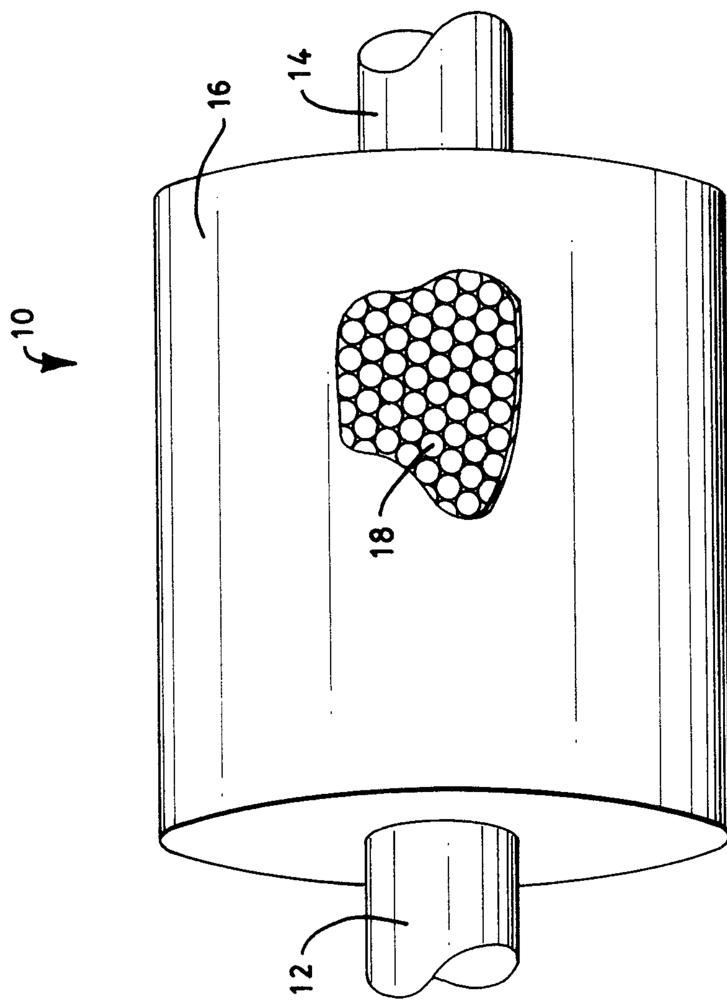

FIG. 1

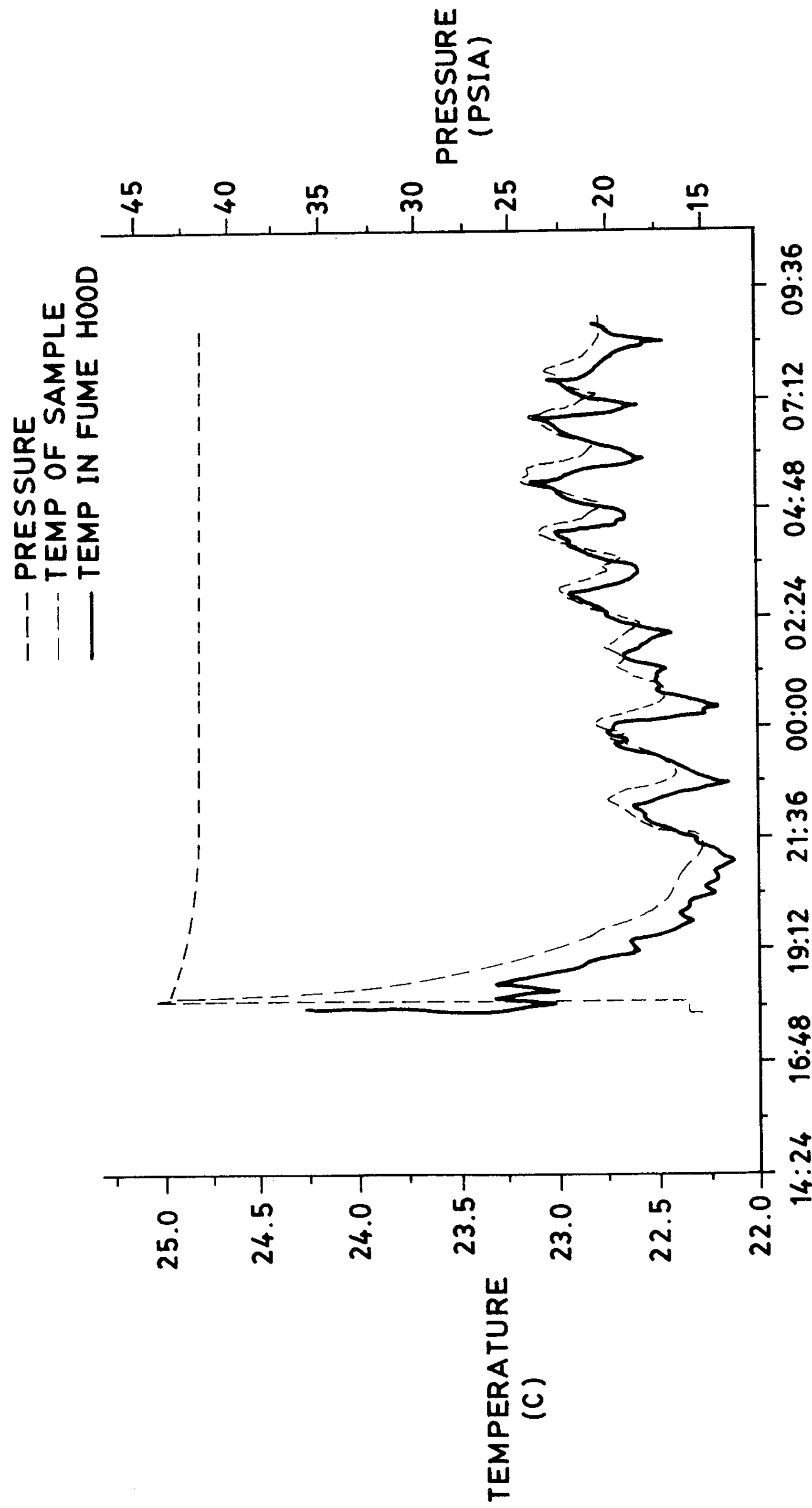

FIG. 2

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/08775

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01B21/083

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 853 148 A (TOM GLENN M ET AL) 1 August 1989 cited in the application see claims 1,4,7	1,2
A	PATENT ABSTRACTS OF JAPAN vol. 014, no. 017 (C-675), 16 January 1990 & JP 01 261209 A (MITSUI TOATSU CHEM INC), 18 October 1989 cited in the application see abstract	1,2
A	PATENT ABSTRACTS OF JAPAN vol. 014, no. 188 (C-0710), 17 April 1990 & JP 02 034506 A (MITSUI TOATSU CHEM INC), 5 February 1990 see abstract	1,2

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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9 July 1999	16/07/1999

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 337 294 A (MITSUI TOATSU CHEMICALS) 18 October 1989 see claims 1,3 -----	2

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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